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[Addressee] Patent Office Director
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[Fee Indication]

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[Submitted Article List]

[Article Name]	Claim	1
[Article Name]	Specification	1
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[Document Name] Claims

[Claim 1] A terminal functional polyolefin represented by the following general formula (I) wherein the weight-average molecular weight (M_w) obtained by gel permeation chromatography (GPC) is 300 or more and the molecular weight distribution (M_w/M_n), which is calculating by dividing the M_w by the number-average molecular weight (M_n), is from 1.0 to 1.7.

X-P-Y (1)

[In the formula (I), X is a hydrogen atom, or a group containing at least one element selected from oxygen, sulfur, nitrogen, phosphorus and halogens, Y is a group containing at least one element selected from oxygen, sulfur, nitrogen, phosphorus and halogens, X and Y may be the same or different, P represents a chain made mainly of an olefin composed only of carbon and hydrogen atoms.]

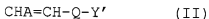
[Claim 2] The terminal functional polyolefin according to claim 1, wherein X is a hydrogen group, and Y is a group containing at least one element selected from oxygen, sulfur, nitrogen, phosphorus and halogens.

[Claim 3] The terminal functional polyolefin according to claim 1 or 2, wherein X and Y are each a group containing at least one element selected from oxygen, sulfur, nitrogen, phosphorus and halogens.

[Claim 4] The terminal functional polyolefin according to any one of claims 1 to 4, which is obtained by carrying out and repeating operations composed of the following steps 1 to 2 and an optional step 3 in any order one or more times in the presence

of an olefin polymerizing catalyst containing a compound (A) which contains a transition metal in the groups IV to V.

[step 1] the step of bringing it into contact with a polar-group-containing olefin (C) represented by the following general formula (II), so as to mix them.



(In the formula (II), Y' is a group containing at least one element from oxygen, sulfur, nitrogen, phosphorus and halogens, Q is an alkylene group which may have a substituent, A represents a hydrogen atom or a hydrocarbon group which may have a substituent, and A may be bonded to Q to form a ring.)

[step 2] the step of bringing the resultant into contact with at least one olefin (D) selected from ethylene and α -olefins having 3 to 20 carbon atoms, and

[step 3] the step of hydrolysis.

[Document Name] Specification

[Title of the Invention] Terminal Functional Polyolefin
and Process for the Production thereof

[Technical Field]

[0001]

The present invention relates to a novel terminal functional polyolefin, and a process for the production thereof.

[Background Art]

[0002]

Polyolefins such as polyethylene (PE) and polypropylene (PP) are light and inexpensive and further have characteristics of having excellent physical properties and workability. On the other hand, high chemical stability of polyolefins is an obstacle for giving, thereto, high functionalities, typical examples of which include printability, paintability, heat resistance and impact resistance, and a function for improving compatibility thereof with other polar polymers. There are known methods for making up for such drawbacks and causing polyolefins to have functionalities. Examples thereof include a method of polymerizing an olefin with a polar monomer such as vinyl acetate or a methacrylic acid ester by radical polymerization; and a method of grafting a polar monomer such as maleic anhydride to a polyolefin in the presence of a peroxide. However, according to these methods, it is generally difficult to control minutely the structure of olefin chain moieties in the resultant polymers. As a result, excellent, original physical properties of polyolefin may be damaged.

[0003]

In general, it is well known that a process using living polymerization is useful as a process for producing such a polymer. In the case of highly-controlled living polymerization, a growing terminal of the polymer quantitatively keeps reactivity. It is therefore known that the reactivity is used to cause the terminal to react directly with a polar-group-containing monomer, whereby a polymer having a functional group at its terminal position can be effectively produced.

[0004]

However, in the case of polymerizing any olefin by living polymerization, chain transfer reaction of the growing polymer chain is frequently caused under ordinary conditions; therefore, it is very difficult to produce an olefin polymer by living polymerization. Some examples wherein an α -olefin is subjected to living polymerization have been reported so far. However, in any one of the examples, the polymerization is conducted at a very low temperature in order to control chain transfer reaction. The polymerization activity thereof is also a low value. The molecular weight thereof is also at most several tens of thousands. Furthermore, monomers that can be polymerized are restricted in many cases. It is particularly difficult to produce industrial important ethylene-based (co) polymers. Out of regularity polymerizations of α -olefins, polymerizations exhibiting a high regularity are hardly known.

[0005]

Under such situations, the Applicant already discloses

a transition metal compound having a salicylaldehyde ligand as a novel catalyst for olefin polymerization (see Patent Document 1), and further suggests a process of using the transition metal compound to produce a novel polar-group-containing block copolymer (see Patent Document 2). However, the two published documents neither disclose any polymer having a polar functional group only at its single terminal or polar functional groups only at both of its terminals, nor any process for the production thereof. The Applicant has eagerly searched processes for producing a terminal functional polymer useful for various purposes, using a catalyst containing a transition metal compound having the above-mentioned salicylaldehyde ligand, and has then made the present invention.

[Patent Document 1] Japanese Patent Application
Laid-Open No. 11-315109

[Patent Document 2] Japanese Patent Application
Laid-Open No. 2003-40953

[Disclosure of the Invention]

[Problems to be Solved by the Invention]

[0006]

Accordingly, the present invention relates to a polyolefin which has a polar functional group at its terminal position and is useful for various purposes; and a process for producing the same.

[Means for Solving the Problems]

[0007]

The terminal functional polyolefin (F) of the present invention is represented by the following general formula (I) wherein the weight-average molecular weight (M_w) obtained by gel permeation chromatography (GPC) is 300 or more and the molecular weight distribution (M_w/M_n), which is calculating by dividing the M_w by the number-average molecular weight (M_n), is from 1.0 to 1.7.

[0008]

X-P-Y (1)

[0009]

[In the formula (I), X is a hydrogen atom, or a group containing at least one element selected from oxygen, sulfur, nitrogen, phosphorus and halogens, Y is a group containing at least one element selected from oxygen, sulfur, nitrogen, phosphorus and halogens, X and Y may be the same or different, P represents a chain made mainly of an olefin composed only of carbon and hydrogen atoms.]

Preferred embodiments of the terminal functional polyolefin (F) are terminal functional polymers (F-1) wherein X is a hydrogen atom, Y is a group containing at least one element selected from oxygen, sulfur, nitrogen, phosphorus and halogens; terminal functional polymers (F-2) wherein X and Y are each a group containing at least one element selected from oxygen, sulfur, nitrogen, phosphorus and halogens, and X and Y are equal to each other; and terminal functional polymers (F-3) wherein X and Y are each a group containing at least one element selected from oxygen, sulfur, nitrogen, phosphorus and halogens, and X

and Y are different from each other.

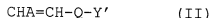
[0010]

The invention also relates to a process for producing the above-mentioned terminal functional polyolefin (F).

Specifically, the terminal functional polyolefin of the invention is a terminal functional polyolefin obtained by carrying out and repeating operations composed of the following steps 1 to 2 and an optional step 3 in any order one or more times in the presence of an olefin polymerizing catalyst containing a compound (A) which contains a transition metal in the groups IV to V.

[step 1] the step of bringing it into contact with a polar-group-containing olefin (C) represented by the following general formula (II), so as to mix them.

[0011]



[0012]

(In the formula (II), Y' is a group containing at least one element from oxygen, sulfur, nitrogen, phosphorus and halogens, Q is an alkylene group which may have a substituent, A represents a hydrogen atom or a hydrocarbon group which may have a substituent, and A may be bonded to Q to form a ring.)

[step 2] the step of bringing the resultant into contact with at least one olefin (D) selected from ethylene and α -olefins having 3 to 20 carbon atoms, and

[step 3] the step of hydrolysis.

[Best Modes for Carrying Out the Invention]

[0013]

The following will describe the terminal functional polyolefin of the present invention, and a process for the production thereof in detail.

Terminal functional polyolefin

The terminal functional polyolefin (F) of the invention is represented by the following general formula (I).

[0014]



[0015]

In the formula (I), X is a hydrogen atom, or a group containing at least one element selected from oxygen, sulfur, nitrogen, phosphorus and halogens. Specific examples of X which is different from a hydrogen atom include an oxy group; a peroxy group; a hydroxyl group; a hydroperoxy group; alkoxy groups such as methoxy, ethoxy, propoxy and butoxy; aryloxy groups such as phenoxy, methylphenoxy, dimethylphenoxy, and naphthoxy; arylalkoxy groups such as phenylmethoxy, and phenylethoxy; an acetoxym group; a carbonyl group; groups wherein an element in the group XIII or XIV is bonded to an oxygen, such as silyloxy, boryloxy, and aluminoxy; an amino group; N-mono-substituted amino groups such as methylamino, N-benzylamino, and N-cyclohexylamino; N,N-di-substituted alkylamino groups such as dimethylamino, diethylamino, dipropylamino, dibutylamino, dicyclohexylamino, dibenzylamino, piperidino, and morpholino;

arylamino or alkylamono groups such as phenylamino, diphenylamino, ditolylamino, dinaphthylamino, and methylphenylamino; N,N-disilyl-substituted amino groups such as N,N-bis(trimethylsilyl)amino, N,N-bis(triethylsilyl)amino, and N,N-bis(t-butyl dimethylsilyl)amino; other nitrogen-containing groups such as imine, amide, imide, ammonium, and nitrile; sulfonate groups such as methylsulfonate, trifluoromethanesulfonate, phenylsulfonate, benzylsulfonate, p-toluenesulfonate, trimethylbenzenesulfonate, triisobutylbenzenesulfonate, p-chlorobenzenesulfonate, and pentafluorobenzenesulfonate; sulfinat groups such as methylsulfinat, phenylsulfinat, benzylsulfinat, p-toluenesulfinat, trimethylbenzenesulfinat, and pentafluorobenzenesulfinat; alkylthio groups; arylthio groups; a sulfate group; a sulfide group; a polysulfide group; and a thiolate group. Examples of the phosphorus-containing group include phosphines such as phenylphosphino, methylphosphino, ethylphosphino, diphenylphosphino, dimethylphosphino, diethylphosphino, methylphenylphosphino, and dibenzylphosphino; phosphine oxides; phosphine sulfides; and phosphorous acids. Examples of the halogens include fluorine, chlorine, bromine, and iodine. Y is a group containing at least one element selected from oxygen, sulfur, nitrogen, phosphorus and halogens. Examples of Y are the same as exemplified as X. P represents a chain made mainly of an olefin composed only of carbon and hydrogen atoms. Such an olefin polymer chain is a polyolefin chain made of structural units

derived from at least one selected from ethylene and α -olefins having 3 to 10 carbon atoms, as will be described later in the item of Production Process.

[0016]

Of terminal functional polyolefins (F) satisfying such requirements, the following are preferred: terminal functional polymers (F-1) wherein X is a hydrogen atom, Y is a group containing at least one element selected from oxygen, sulfur, nitrogen, phosphorus and halogens; terminal functional polymers (F-2) wherein X and Y are each a group selected from groups containing at least one element selected from oxygen, sulfur, nitrogen, phosphorus and halogens, and X and Y are equal to each other; and terminal functional polymers (F-3) wherein X and Y are each a group containing at least one element selected from oxygen, sulfur, nitrogen, phosphorus and halogens, and X and Y are different from each other. Of the single terminal functional olefins (F-1), terminal functional polyolefins wherein Y is a hydroxyl group and an amino group are particularly preferred. Of the both-terminal functional polyolefins (F-2), terminal functional polyolefins wherein both of X and Y are hydroxyl groups, or wherein X is a hydroxyl group and Y is an amino group are particularly preferred.

[0017]

Production Process

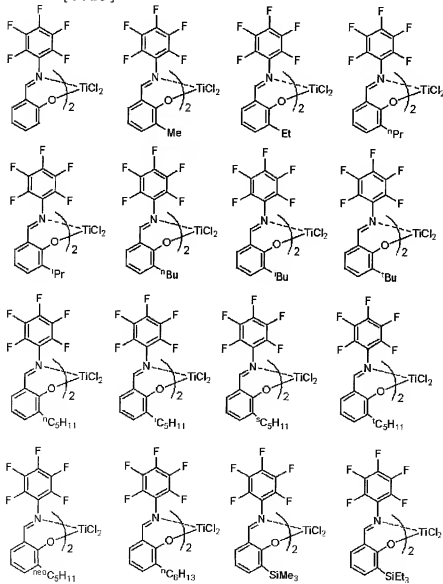
The terminal functional polyolefin of the invention can be effectively obtained by carrying out steps which will be detailed below successively in the presence of an olefin

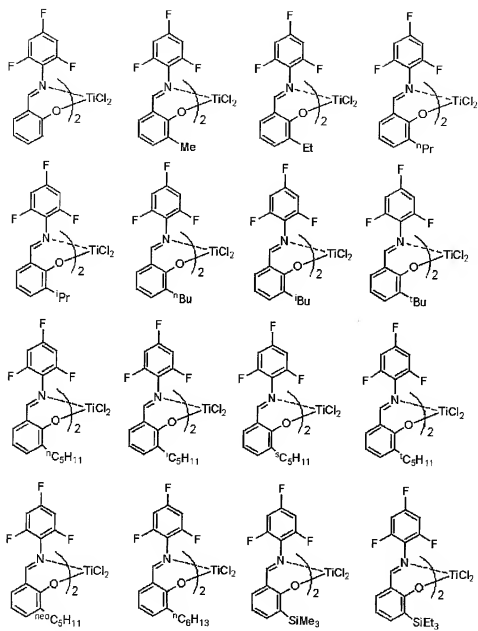
polymerizing catalyst containing a compound (A) which contains a transition metal in the groups IV to V in the periodic table.

[0018]

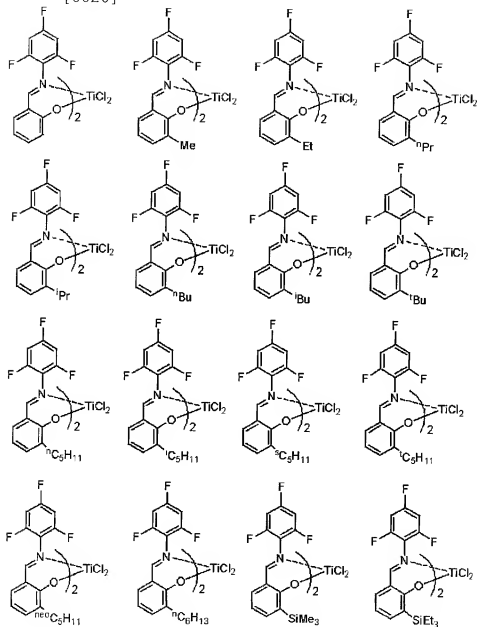
As the group IV to V transition metal containing compound (A), transition metal compounds described in the above-mentioned Patent Document 2, which was filed by the Applicant, can be used without any limitation. Of these transition metal compounds, preferred transition metal compounds are illustrated below.

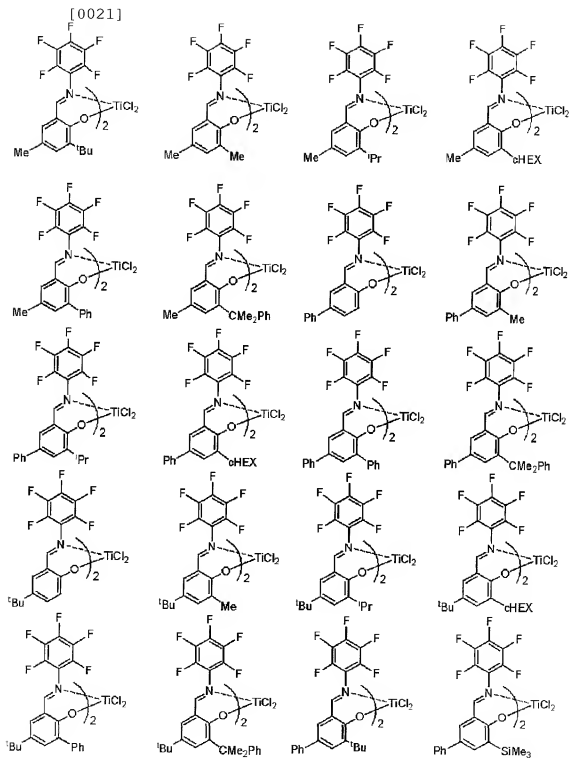
[0019]





[0020]





[0022]

In the production process according to the invention, an organic aluminum oxy compound (B) can be used together with the group IV to V transition metal containing compound (A). The organic aluminum oxy compound (B) may be an aluminoxane known in the prior art, or an organic aluminum oxy compound insoluble in benzene, as exemplified in Japanese Patent Application Laid-Open No. 2-78687.

[0023]

The known aluminoxane can be produced by, for example, a process as described below, and is usually obtained as a solution containing a solvent of a hydrocarbon.

(1) A process of adding an organic aluminum compound, such as trialkylaluminum, to a suspension of a compound containing absorbed water or a salt containing crystal water, such as magnesium chloride hydrate, copper sulfate hydrate, aluminum sulfate hydrate, nickel sulfate hydrate or cerium (I) chloride hydrate, in a hydrocarbon medium, so as to cause the absorbed water or crystal water to react with the organic aluminum compound.

(2) A process of causing water, ice or water vapor to act directly on an organic aluminum compound, such as trialkylaluminum, in a solvent such as benzene, toluene, ethyl ether or tetrahydrofuran.

(3) A process of causing an organic tin compound such as dimethyltin oxide or dibutyltin oxide to react with an organic

aluminum compound, such as trialkylaluminum, in a solvent such as decane, benzene or toluene.

[0024]

Specific examples of the organic aluminum compound used when the aluminosilane is prepared include tri-n-alkylaluminums such as trimethylaluminum, triethylaluminum, tri-n-butylaluminum, tripropylaluminum, triisopropylaluminum, trihexylaluminum, and trioctylaluminum; branched-trialkyl aluminums such as triisobutylaluminum, tri-sec-butylaluminum, and tri-2-ethylhexylaluminum; tricycloalkylaluminums such as tricyclohexylaluminum, and tricyclooctylaluminum; triarylaluminums such as triphenylaluminum, and tritolylaluminum; and trialkenylaluminums such as triisoprenylaluminum represented by $(i-C_4H_9)_xAl_y(C_5H_{10})_z$, wherein x, y and z are each a positive number and $z \geq 2x$. Of these, trialkylaluminums and tricycloalkylaluminums are preferred and trimethylaluminum is particularly preferred. The above-mentioned organic aluminum compounds may be used alone or in combination of two or more thereof.

[0025]

In the production process according to the invention, at least one selected from the following can be caused to be present together with the group IV to V transition metal containing compound (A) and the organic aluminum oxy compound (B): an organic metal compound, a compound which can react with the transition metal compound (A) to form an ion pair, a carrier, and an organic

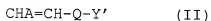
compound. About the four components used if necessary, ones described in the above-mentioned Patent Document 2 can be used without any limitation.

[0026]

The terminal functional polyolefin (F) of the invention can be effectively produced by carrying out and repeating operations composed of the following steps 1 to 2 and an optional step 3 in any order one or more times.

[step 1] the step of bringing it into contact with a polar-group-containing olefin (C) represented by the following general formula (II), so as to mix them.

[0027]



[0028]

(In the formula (II), Y' is a group containing at least one element from oxygen, sulfur, nitrogen, phosphorus and halogens, Q is an alkylene group which may have a substituent, A represents a hydrogen atom or a hydrocarbon group which may have a substituent, and A may be bonded to Q to form a ring.)

[step 2] the step of bringing the resultant into contact with at least one olefin (D) selected from ethylene and α -olefins having 3 to 20 carbon atoms, and

[step 3] the step of hydrolysis.

Y' in the general formula (II) used in the step 1 is a group containing at least one element from oxygen, sulfur, nitrogen, phosphorus and halogens. Examples of such a group include an oxy group; a peroxy group; a hydroxyl group; a

hydroperoxy group; alkoxy groups such as methoxy, ethoxy, propoxy and butoxy; aryloxy groups such as phenoxy, methylphenoxy, dimethylphenoxy, and naphthoxy; arylalkoxy groups such as phenylmethoxy, and phenylethoxy; an acetoxy group; a carbonyl group; groups wherein an element in the group XIII or XIV is bonded to an oxygen, such as silyloxy, boryloxy, and aluminioxy; an amino group; N-mono-substituted amino groups such as methylamino, N-benzylamino, and N-cyclohexylamino; N,N-di-substituted alkylamino groups such as dimethylamino, diethylamino, dipropylamino, dibutylamino, dicyclohexylamino, dibenzylamino, piperidino, and morpholino; arylamino or alkylamino groups such as phenylamino, diphenylamino, ditolylamino, dinaphthylamino, and methylphenylamino; N,N-disilyl-substituted amino groups such as N,N-bis(trimethylsilyl)amino, N,N-bis(triethylsilyl)amino, and N,N-bis(t-butyl)dimethylsilyl)amino; other nitrogen-containing groups such as imine, amide, imide, ammonium, and nitrile; sulfonate groups such as methylsulfonate, trifluoromethanesulfonate, phenylsulfonate, benzylsulfonate, p-toluenesulfonate, trimethylbenzenesulfonate, triisobutylbenzenesulfonate, p-chlorobenzenesulfonate, and pentafluorobenzenesulfonate; sulfinates groups such as methylsulfinates, phenylsulfinates, benzylsulfinates, p-toluenesulfinates, trimethylbenzenesulfinates, and pentafluorobenzenesulfinates; alkylthio groups; arylthio groups; a sulfate group; a sulfide group; a polysulfide group; and a thiolate group. Examples of the phosphorus-containing

group include phosphines such as phenylphosphino, methylphosphino, ethylphosphino, diphenylphosphino, dimethylphosphino, diethylphosphino, methylphenylphosphino, and dibenzylphosphino; phosphine oxides; phosphine sulfides; and phosphorous acids. Examples of the halogens include fluorine, chlorine, bromine, and iodine. Of these, preferred are silyloxy, aluminoxy, boryloxy, and N,N-disilyl-substituted amino groups, which do not poison the catalyst easily and which generate active hydrogen after hydrolysis after the end of the step 2.

[0029]

In the general formula (II), Q is an alkylene group which may have a substituent. Q is usually an alkylene group which may have a substituent wherein the total number of carbon atoms is from 2 to 20. Of alkylene groups having such a requirement, an unsubstituted linear alkylene group represented by the following formula (IV) is preferably used

[0030]

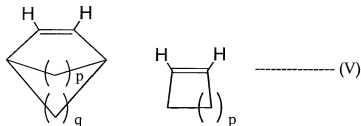


[0031]

(In the formula (IV), n is a positive integer of 1 to 15.)

In the general formula (II), A represents a hydrogen atom or a hydrocarbon group which may have a substituent, and A may be bonded to Q to form a ring. Of structures satisfying such requirements, any cycloolefin represented by the following formula (V) is preferably used.

[0032]



[0033]

(In the formula (V), p represents an integer of 1 to 10, and is bonded to Y at any position, q is an integer of 0 to 10, and when q is 0, the cycloolefin is a monocycloolefin.)

Examples of the α -olefin having 3 to 20 carbon atoms, used in the step 2, include linear or branched α -olefins having 3 to 20 carbon atoms, such as propylene, 1-butene, 2-butene, 1-pentene, 3-methyl-1-butene, 1-hexene, 4-methyl-1-pentene, 3-methyl-1-pentene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene, and 1-eicocene; and cyclic olefins having 3 to 20 carbon atoms, such as cyclopentene, cycloheptene, norbornene, 5-methyl-2-norbornene, tetracyclododecene, and 2-methyl 1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene. Other examples of the olefin having 3 to 20 carbon atoms include vinylcyclohexane, dienes and polyenes. Additional examples of the olefin include aromatic vinyl compounds styrene, o-methylstyrene, m-methylstyrene, p-methylstyrene, o,p-dimethylstyrene, o-ethylstyrene, m-ethylstyrene, and p-ethylstyrene, and other mono- or poly-alkylstyrenes; and 3-phenylpropylene, 4-phenylbutene, and α -methylstyrene. These olefins may each contain in the molecule thereof a

heteroatom such as an oxygen, nitrogen, or silicon atom. The olefins may be used alone or in combination of two or more thereof.

[0034]

The terminal functional polyolefin (F) according to the invention is characterized by carrying out and repeating the above-mentioned two steps one or more times.

[0035]

It will be specifically described hereinafter.

[0036]

When operations composed of the steps 1 to 2 and the optional step 3, for example, the steps 1 and 2 are performed one time in any order, the single-terminal functional polyolefin (F1), which is the first preferred embodiment of the terminal functional polyolefin (F) of the invention, can be efficiently produced. When the above-mentioned operations are performed in order of the steps 1, 2 and 1, and the optional step 3, the both-terminal functional polyolefin (F2), which is the second preferred embodiment, can be effectively produced.

[0037]

In the case that the both-terminal functional polyolefin (F2) is produced, the two groups X and Y in the both-terminal functional polyolefin to be produced can be made different from each other when the polar-group-containing olefin (C) used in the first and second [steps 1] can be made different in kind (that is, the polar-group-containing olefin (C) represented by the general formula (II) wherein Z is an oxygen atom and that wherein Z is a nitrogen atom are used.

[0038]

In the case that the olefins (D) used in the first and second [steps 2] are made different from each other in kind in the production of the both-terminal functional polyolefin (F2), the olefin chain (P moiety) in the terminal functional polyolefin (F) represented by the general formula (I) can be rendered a block type chain composed of two kinds of olefin chains. For example, when the olefin (D) used in the first step 2 is ethylene and the olefin (D) used in the second step 2 is propylene, the resultant terminal functional polyolefin is represented by the following (IV).

[0039]

X-PE-PP-Y (IV)

[0040]

(In the formula (IV), X and Y have the same meanings as in the formula (I), and PE and PP represent a polyethylene chain and a polypropylene chain, respectively.)

In the invention, the polymerization can be carried out by any one of liquid-phase polymerizations, such as dissolution polymerization, suspension polymerization, and gas-phase polymerizations.

[0041]

Specific examples of an inert hydrocarbon medium used in the liquid-phase polymerization include aliphatic hydrocarbons such as propane, butane, pentane, hexane, heptane, octane, decane, dodecane, and kerosene; alicyclic hydrocarbons such as cyclopentane, cyclohexane, and methylcyclopentane; aromatic

hydrocarbons such as benzene, toluene, and xylene; halogenated hydrocarbons such as ethylene chloride, chlorobenzene, and dichloromethane; and mixtures thereof. The olefin itself can be used as the solvent.

[0042]

When the terminal functional polyolefin according to the invention is produced in the presence of the above-mentioned catalyst, the operations composed of the steps 1 and 2 are usually carried out without isolating any product in each of the steps. Usually, the catalyst is once charged when the initial step 1 is started. The group IV to V transition metal compound (A) is used in an amount ranging usually from 10^{-12} to 10^0 mole, preferably from 10^{-10} to 10^{-1} mole per liter of the reaction volume. The organic aluminum oxy compound (B) is used in such an amount that the mole ratio of aluminum atoms in the component (B) to transition metal atoms (M) in the transition metal compound (A) (Al/M) will be a value ranging usually from 10 to 500,000, preferably from 50 to 100,000.

[0043]

When an organic metal compound, a compound which can react with the transition metal compound (A) to form an ion pair, a carrier and an organic compound, as other optional components, are used together, the used amounts thereof are amounts described in the Patent Document 1.

[0044]

The step 1 can be finished by the contact usually at -20 to 50°C , preferably at 0 to 25°C for 1 to 300 minutes, preferably

for 20 to 200 minutes.

[0045]

In the step 2, the polymerization reaction is advanced by the contact usually at -20 to 75°C , preferably at -0 to 50°C for 1 to 600 minutes, preferably for 5 to 180 minutes. The pressure in the step 2 is usually from a normal pressure to 100 kg/cm^2 , preferably from a normal pressure to 50 kg/cm^2 . The polymerization reaction can be conducted by any one of batch type, semi-continuous type, and continuous type processes. The polymerization can be conducted at two or more separated stages wherein reaction conditions are different.

[0046]

The terminal functional polyolefin of the invention can be developed into various applications. The polyolefin can be applied to, for example, a high molecular weight additive; a compatibility accelerator; a diblock copolymer useful as a compatibility accelerator or modifier for polymer; a precursor of a triblock copolymer useful as thermoplastic elastomer or the above-mentioned articles; or a surface modifier for improving paintability, adhesive property and other properties of resin. The polyolefin can be used, in the form of a macromonomer, as raw material of a polymer having a specific structure such as a comb-shaped or star-shaped structure, and applied to a viscosity adjustor for oil, or some other article.

[0047]

In the hydrolysis step of the step 3, which is an optional constituting requirement of the production process according

to the invention, water or alcohol is usually used as a hydrolyzing agent, and the hydrolysis is conducted under an acidic or basic condition. The hydrolysis may be conducted in the presence of an organic solvent in a two-phase system, or conducted in a gas phase using steam. Usually, the following conditions are adopted: a temperature of 0 to 800°C and a time of 1 minute to 24 hours.

[0048]

The invention will be specifically described on the basis of examples hereinafter. However, the invention is not limited to these examples. The structures of polymers obtained in the examples were each decided by use of NMR (FT: 270 MHz, ^1H ; and 67.5 MHz, ^{13}C), DSC, high-temperature GPC, and so on.

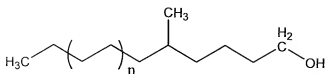
[Example 1]

[0049]

Into a glass reactor having an internal volume of 500 mL and purged sufficiently with nitrogen were charged 250 mL of toluene and 15.2 mmol of methylaluminoxane, the amount being an amount in terms of aluminum atoms therein. Thereto was added a solution of 21.3 mg (0.136 mmol) of $\text{Me}_2\text{AlO}-(\text{CH}_2)_4\text{CH}=\text{CH}_2$ in toluene. Thereto was added a solution of 88.9 mg (containing the weight of diethyl ether, 0.101 mmol) of a titanium complex, bis[N-(3-*t*-butylsalicylidene)-2,3,4,5,6-pentafluoroanilinato]titanium dichloride in toluene, and then the components were caused to react at 27°C for 15 minutes. Thereafter, the reaction solution was cooled to 0°C. Thereafter, a mixed gas of ethylene

and nitrogen (gas flow rate: ethylene, 5 L/h; and nitrogen, 50 L/h), the pressure of which was a normal pressure, was blown from the bottom of the reactor to the inside thereof so as to cause the components to react at 0°C for 5 minutes. Thereafter, the supply of ethylene was stopped and methanol was added thereto, thereby terminating the polymerization. After the termination of the polymerization, the reactant was poured into 600 mL of methanol containing a small amount of hydrochloric acid to precipitate the entire amount of a polymer. The polymer was collected by filtration. The polymer was dried at 80°C under a reduced pressure for 10 hours so as to be yielded in an amount of 0.266 g. The polymerization activity per mmol of titanium was 30.9 g, and the melting peak temperature based on DSC was 133.8°C. In the ^1H NMR spectrum (FT: 270 MHz in $\text{C}_2\text{D}_2\text{Cl}_4$ at 120°C) of this polymer, a triplet corresponding to a methylene group adjacent to an OH group made its appearance near 3.64 ppm, and an overlap of methyl groups of two types at terminals made its appearance near 0.95 ppm. The integration ratio therebetween was 2:6. In the ^{13}C NMR spectrum (FT: 67.5 MHz in $\text{C}_2\text{D}_2\text{Cl}_4$ at 120°C), the methyl groups made their appearance at 14.2 ppm and 20.0 ppm, respectively, and a signal corresponding to the methylene group adjacent to the OH group made its appearance at 63.3 ppm. From the above, a structure of a polymer of the following formula was identified:

[0050]



[Example 2]

[0051]

Into a glass reactor having an internal volume of 500 mL and purged sufficiently with nitrogen were charged 250 mL of toluene and 10.0 mmol of methylaluminoxane, the amount being an amount in terms of aluminum atoms therein. The reaction solution was cooled to 0°C, and then thereto was added a solution of 10.7 mg (0.0685 mmol) of $\text{Me}_2\text{AlO}-(\text{CH}_2)_4\text{CH}=\text{CH}_2$ in toluene. Thereto was added a solution of 58.4 mg (containing the weight of diethyl ether, 0.0666 mmol) of a titanium complex, bis[N-(3-t-butylsalicylidene)-2,3,4,5,6-pentafluoroanilinate]titanium dichloride in toluene, and then the components were caused to react at 0°C for 30 minutes. Thereafter, propylene (gas flow rate: 100 L/h), the pressure of which was a normal pressure, was blown from the bottom of the reactor to the inside thereof so as to cause the components to react at 0°C for 105 minutes. Thereafter, the supply of propylene was stopped, and methanol was added thereto, thereby terminating the polymerization. After the termination of the polymerization, the reactant was poured into 600 mL of methanol containing a small amount of hydrochloric acid to precipitate the entire amount of a polymer. The polymer was collected by filtration. The polymer was dried at 80°C under a reduced pressure for 10 hours so as to be yielded in an amount of 0.354 g. The polymerization activity per mmol of titanium was 3.04 g, the weight-average molecular weight (Mw) of the polymer was 9,260,

the ratio of the weight-average molecular weight to the number-average molecular weight (M_n) was 1.05, and the melting peak temperature based on DSC was 144.4°C. In the ^1H NMR spectrum (FT: 270 MHz in $\text{C}_2\text{D}_2\text{Cl}_4$ at 120°C) of this polymer, a triplet corresponding to a methylene group adjacent to an OH group made its appearance near 3.64 ppm. In the ^{13}C NMR spectrum (FT: 67.5 MHz in $\text{C}_2\text{D}_2\text{Cl}_4$ at 120°C), a signal corresponding to the methylene group adjacent to the OH group made its appearance at 63.3 ppm. Peaks at 22.5–24.0 ppm corresponding to isopentyl and isobutyl groups, which were unreacted initiating ends, hardly made their appearance.

[Example 3]

[0052]

Propylene was polymerized under the same conditions as in Example 2 except that $\text{Me}_2\text{AlO}-(\text{CH}_2)_9\text{CH}=\text{CH}_2$ was used instead of $\text{Me}_2\text{AlO}-(\text{CH}_2)_4\text{CH}=\text{CH}_2$. The polymerization activity per mmol of titanium was 3.03 g. In the ^1H NMR spectrum (FT: 270 MHz in $\text{C}_2\text{D}_2\text{Cl}_4$ at 120°C) of this polymer, a triplet corresponding to a methylene group adjacent to an OH group made its appearance near 3.64 ppm.

[Example 4]

[0053]

Propylene was polymerized under the same conditions as in Example 2 except that $\text{Me}_3\text{SiO}-(\text{CH}_2)_9\text{CH}=\text{CH}_2$ was used instead

of $\text{Me}_2\text{AlO}-(\text{CH}_2)_4\text{CH}=\text{CH}_2$. The polymerization activity per mmol of titanium was 2.88 g, the weight-average molecular weight (M_w) of the polymer was 9,250, the ratio of the weight-average molecular weight to the number-average molecular weight (M_n) was 1.06, and the melting peak temperature based on DSC was 142.0°C. In the ^1H NMR spectrum (FT: 270 MHz in $\text{C}_2\text{D}_2\text{Cl}_4$ at 120°C) of this polymer, a triplet corresponding to a methylene group adjacent to an OH group made its appearance near 3.64 ppm.

[Example 5]

[0054]

Into a glass reactor having an internal volume of 500 mL and purged sufficiently with nitrogen were charged 250 mL of toluene and 7.95 mmol of methylaluminoxane, the amount being an amount in terms of aluminum atoms therein. Thereto was added a solution of 20.9 mg (0.0862 mmol) of $\text{Me}_3\text{SiO}-(\text{CH}_2)_9\text{CH}=\text{CH}_2$ in toluene. Thereto was added a solution of 69.8 mg (containing the weight of diethyl ether, 0.0795 mmol) of a titanium complex, bis[N-(3-t-butylsalicylidene)-2,3,4,5,6-pentafluoroanilinate]titanium dichloride in toluene, and then the components were caused to react at 25°C for 5 minutes. Thereafter, the reaction solution was cooled to 0°C. Thereafter, propylene (gas flow rate: 100 L/h), the pressure of which was a normal pressure, was blown from the bottom of the reactor to the inside thereof so as to cause the components to react at 0°C for 90 minutes. Thereafter, the supply of propylene was stopped, and then the reaction solution was heated to room temperature while nitrogen

(gas flow rate: 50 L/h) was caused to flow thereinto. Thereto was added a solution of 113.3 mg (0.4673 mmol) of $\text{Me}_3\text{SiO}-(\text{CH}_2)_9\text{CH}=\text{CH}_2$ in toluene, and then the components were caused to react for 1 hour. Thereafter, thereto was added methanol to terminate the polymerization. After the termination of the polymerization, the reactant was poured into 600 mL of methanol containing a small amount of hydrochloric acid to precipitate the entire amount of a polymer. The polymer was collected by filtration. The polymer was dried at 80°C under a reduced pressure for 10 hours so as to be yielded in an amount of 0.317 g. The polymerization activity per mmol of titanium was 2.65 g, the weight-average molecular weight (M_w) of the polymer was 10,280, the ratio of the weight-average molecular weight to the number-average molecular weight (M_n) was 1.08, and the melting peak temperature based on DSC was 143.0°C. In the ^1H NMR spectrum (FT: 270 MHz in $\text{C}_2\text{D}_2\text{Cl}_4$ at 120°C) of this polymer, a triplet corresponding to methylene groups adjacent to OH groups made its appearance near 3.64 ppm. The ratio between the triplet and the sum of main peaks of the polymer was 2:681. The number-average molecular weight (M_n) based on GPC was 9,560. From these matters, it is understood that two functional groups were introduced per polymer chain. In the ^{13}C NMR spectrum (FT, 67.5 MHz, in $\text{C}_2\text{D}_2\text{Cl}_4$, at 120°C), a signal corresponding to methylene groups adjacent to OH groups made its appearance at 63.3 ppm. Peaks at 22.5–24.0 ppm corresponding to isopentyl and isobutyl groups, which were unreacted initiating and terminating ends, and a peak (near 14 ppm) originating from any

n-propyl group hardly made their appearance. It is understood from the above that both-terminal functional syndiotactic polypropylene was synthesized.

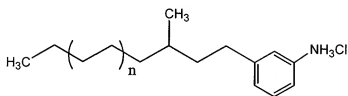
[Example 6]

[0055]

Into a glass reactor having an internal volume of 500 mL and purged sufficiently with nitrogen were charged 250 mL of toluene and 4.82 mmol of methylaluminoxane, the amount being an amount in terms of aluminum atoms therein. Thereto was added a solution of 15.5 mg (0.0532 mmol) of $(\text{Me}_3\text{Si})_2\text{N}-m-\text{C}_6\text{H}_4-(\text{CH}_2)_2\text{CH}=\text{CH}_2$ in toluene. Thereto was added a solution of 42.3 mg (containing the weight of diethyl ether, 0.0482 mmol) of a titanium complex, bis[N-(3-t-butylsalicylidene)-2,3,4,5,6-pentafluoroanilinate]titanium dichloride in toluene, and then the components were caused to react at 0°C for 120 minutes. Thereafter, a mixed gas of ethylene and nitrogen (gas flow rate: ethylene, 5 L/h; and nitrogen, 50 L/h), the pressure of which was a normal pressure, was blown from the bottom of the reactor to the inside thereof so as to cause the components to react at 0°C for 3.5 minutes. Thereafter, the supply of ethylene was stopped and methanol was added thereto, thereby terminating the polymerization. After the termination of the polymerization, the reactant was poured into 600 mL of methanol containing a small amount of hydrochloric acid to precipitate the entire amount of a polymer. The polymer was collected by filtration. The polymer was dried at 80°C under

a reduced pressure for 10 hours so as to be yielded in an amount of 0.148 g. The polymerization activity per mmol of titanium was 52.5 g. In the ^1H NMR spectrum (FT, 270 MHz, in $\text{C}_2\text{D}_2\text{Cl}_4$, at 120°C) of this polymer, a triplet corresponding to a methylene group adjacent to a phenyl group, aromatic protons, and an overlap of methyl groups of two types at terminals made their appearance near 2.53 ppm, 6.45–6.65 ppm and 7–7.13 ppm, respectively, at an integration ratio of 2:4:6 near 0.95 ppm. From the above, a structure of a polymer of the following formula was identified.

[0056]



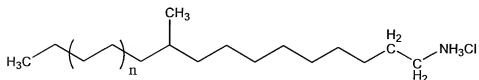
[Example 7]

[0057]

Into a glass reactor having an internal volume of 500 mL and purged sufficiently with nitrogen were charged 250 mL of toluene and 6.48 mmol of methylaluminoxane, the amount being an amount in terms of aluminum atoms therein. Thereto was added a solution of 21.0 mg (0.0669 mmol) of $(\text{Me}_3\text{Si})_2\text{N}-(\text{CH}_2)_9\text{CH}=\text{CH}_2$ in toluene. Thereto was added a solution of 56.8 mg (containing the weight of diethyl ether, 0.0647 mmol) of a titanium complex, bis[N-(3-*t*-butylsalicylidene)-2,3,4,5,6-pentafluoroanilinate]titanium dichloride in toluene, and then the components were caused to react at 0°C for 150 minutes. Thereafter, a mixed gas of ethylene and nitrogen (gas flow rate: ethylene, 5 L/h;

and nitrogen, 50 L/h), the pressure of which was a normal pressure, was blown from the bottom of the reactor to the inside thereof so as to cause the components to react at 0°C for 3 minutes. Thereafter, the supply of ethylene was stopped and methanol was added thereto, thereby terminating the polymerization. After the termination of the polymerization, the reactant was poured into 600 mL of methanol containing a small amount of hydrochloric acid to precipitate the entire amount of a polymer. The polymer was collected by filtration. The polymer was dried at 80°C under a reduced pressure for 10 hours so as to be yielded in an amount of 0.143 g. The polymerization activity per mmol of titanium was 44.1 g. In the ^1H NMR spectrum (FT, 270 MHz, in $\text{C}_2\text{D}_2\text{Cl}_4$, at 120°C) of this polymer, a triplet corresponding to a methylene group adjacent to a NH_3Cl group, a multiplet corresponding to a methylene group adjacent thereto, and an overlap of methyl groups of two types at terminals made their appearance near 3 ppm, 1.80 ppm and 0.95 ppm, respectively, at an integration ratio of 2:2:6. From the above, a structure of a polymer of the following formula was identified:

[0058]



[0059]

[Comparative Example 1]

Propylene was polymerized under the same conditions as

in Example 2 except that $\text{Me}_2\text{AlO}-(\text{CH}_2)_4\text{CH}=\text{CH}_2$ was not added. The polymerization activity per mmol of titanium was 3.16 g, and the melting peak temperature based on DSC was 146.0°C. In the ^1H NMR spectrum (FT, 270 MHz, in $\text{C}_2\text{D}_2\text{Cl}_4$, at 120°C) of this polymer, no peak made its appearance near 3.64 ppm. In the ^{13}C NMR spectrum (FT, 67.5 MHz, in $\text{C}_2\text{D}_2\text{Cl}_4$, at 120°C), peaks at 22.5-24.0 ppm corresponding to isopentyl and isobutyl groups at the terminals made their appearance.

[Industrial Applicability]

[0060]

About the polyolefin having a polar functional group at its single terminal position or having polar functional groups at both of its terminal positions, the polyolefin itself, or the polyolefin subjected to a further modifying treatment is useful for various purposes.

[Document Name] Abstract

[Summary]

[Object] Provided are a polyolefin which has a polar functional group at its terminal and is useful for various purposes and a process for the production thereof.

[Solving Means] A terminal functional polyolefin represented by the following general formula (I) wherein the weight-average molecular weight (M_w) obtained by gel permeation chromatography (GPC) is 300 or more and the molecular weight distribution (M_w/M_n), which is calculating by dividing the M_w by the number-average molecular weight (M_n), is from 1.0 to 1.7.



[In the formula (I), X is a hydrogen atom, or a group containing at least one element selected from oxygen, sulfur, nitrogen, phosphorus and halogens, Y is a group containing at least one element selected from oxygen, sulfur, nitrogen, phosphorus and halogens, X and Y may be the same or different, P represents a chain made mainly of an olefin composed only of carbon and hydrogen atoms.]